

**FABRICATION OF Bi_2Te_3 AND PbTe BASED
THERMOELECTRIC MATERIALS USING HOT PRESSED
METHOD AND ITS SEEBECK COEFFICIENT UNDER LARGE
TEMPERATURE DIFFERENCE**

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ABSTRAK

Bahan termoelektrik berguna dalam menukar sisa haba kepada elektrik selagi wujudnya perbezaan suhu (ΔT). Bahan termoelektrik (TE) berasaskan bismuth telluride (Bi_2Te_3) dan plumbum telluride (PbTe) adalah bahan terancang pada julat suhu rendah dan sederhana 300-500 K dan 500-900 K, masing-masing. Pekali Seebeck ialah salah satu sifat termoelektrik yang menentukan prestasinya melalui angka-merit (ZT) tanpa dimensi. Kaedah fabrikasi biasa bahan TE adalah menggunakan pensinteran plasma percikan (SPS) di bawah tekanan tinggi (20-50 MPa), suhu (773-1373 K) dan di bawah aliran arus kerana output prestasi tinggi dan masa yang singkat (5-30 minit). Namun, peralatan tersebut tidak terdapat di Malaysia. Sebaliknya, ukuran Seebeck yang dibuat secara konvensional menggunakan probe panas diukur di bawah perbezaan suhu kecil ($s\Delta T$) yang tidak mewakili keadaan sebenar operasi bahan. Oleh itu, kajian ini adalah untuk menyiasat kaedah fabrikasi alternatif menggunakan mesin penekan panas yang tersedia secara meluas dan mengkaji kelakuan Seebecknya di bawah perbezaan suhu yang besar ($l\Delta T$). Empat jenis sampel sasaran telah dibuat menggunakan kaedah ini, iaitu $n\text{-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, $n\text{-PbTe}_{0.8}\text{Se}_{0.2}$, $p\text{-Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3$ dan $p\text{-Pb}_{0.4}\text{Sn}_{0.6}\text{Te}$. Dua kaedah penyediaan sampel telah dikaji, menggunakan kaedah nisbah jisim atom dan isipadu. Dalam kaedah jisim atom, jumlah berat molekul sebatian dikira diikuti dengan peratusan jisim setiap bahan untuk mendapatkan jumlah ketumpatan sebatian. Kemudian, jumlah jisim serbuk sebatian dikira untuk menghasilkan jisim setiap bahan. Manakala dalam kaedah nisbah isipadu, ketumpatan setiap bahan dalam sebatian digunakan untuk mengira jumlah yang diperlukan setiap sebatian. Sampel kemudian dimampatkan di bawah tekanan, suhu dan masa yang berbeza-beza untuk mendapatkan pengoptimuman. Komposisi sampel telah disahkan menggunakan Spektroskopi Penyebaran Tenaga (EDS) manakala Seebeck dan rintangan sampel diukur menggunakan probe panas dalaman dan probe 4 mata. Kajian ini berjaya menghasilkan bahan termoelektrik pukal berasaskan Bi_2Te_3 dan PbTe menggunakan kaedah penekan panas. Sampel menggunakan pengiraan jisim atom (AM) menunjukkan nisbah komposisi yang paling hampir $n\text{-Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$, $p\text{-Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$, $n\text{-Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$ dan $p\text{-Pb}_{0.7}\text{Sn}_{0.2}\text{Te}_{1.1}$ yang direka di bawah tekanan dan masa penahanan 13 MPa dan 17 minit pada suhu 423 K dan 493 K masing-masing. Seebeck untuk $n\text{-Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$ pada suhu bilik ialah $-53 \mu\text{V/K}$ yang memberikan 65% lebih rendah berbanding komposisi literatur $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ tetapi sampel $n\text{-Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$ memberikan Seebeck yang serupa daripada $-249 \mu\text{V/K}$. Keputusan yang sama diperolehi bagi kedua-dua sampel $p\text{-Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$ dan $p\text{-Pb}_{0.5}\text{Sn}_{0.2}\text{Te}_{1.1}$ yang menunjukkan perbezaan yang ketara dalam $l\Delta T$ berbanding $s\Delta T$ literatur. Sebaliknya, semua sampel menunjukkan kerintangan elektrik yang lebih tinggi sedikit daripada dalam literatur juga telah dibincangkan. Dapat disimpulkan bahawa bahan termoelektrik boleh dibuat menggunakan kaedah penekan panas sebagai kaedah alternatif dengan kos yang lebih rendah. Walaupun prestasinya lebih rendah daripada kaedah SPS, ia boleh dipertingkatkan dengan meningkatkan suhu, tekanan dan masa. Implikasi kajian ini boleh menggalakkan kajian

bahan termoelektrik berprestasi tinggi di Malaysia dan membangunkan minat dalam pemulihan haba sisa.



ABSTRACT

Thermoelectric material is useful in converting heat waste to electricity as long there is exist of temperature difference (ΔT). Bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) based thermoelectric (TE) materials are state-of-art materials at a low and medium temperature range of 300 – 500 K and 500 – 900 K, respectively. Seebeck coefficient is one of the thermoelectric properties that determine its performance through dimensionless figure-of-merit (ZT). The common fabrication method of TE materials is using the spark plasma sintering (SPS) under high pressure (20 to 50 MPa), temperature (773 to 1373 K) and under the flow of current due to its high performances output and a short time (5 to 30 minutes). However, the equipment is not available in Malaysia. On the other hand, the measurement of Seebeck conventionally made using a hot probe is measured under a small temperature difference ($s\Delta T$) which doesn't represent the real condition of operation of the material. Therefore, this study is to investigate an alternative fabrication method using a widely available hot press machine and study its Seebeck behaviour under large temperature differences (ΔT). Four target types of samples were made using this method, which is n- $\text{Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$, n- $\text{Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$, p- $\text{Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$ and p- $\text{Pb}_{0.5}\text{Sn}_{0.2}\text{Te}_{1.1}$. Two methods of preparation of sample were studied, using atomic mass and volume ratio method. In the atomic mass method, the total molecular weight of the compound was calculated followed by the percentage mass of each material to get the total density of the compound. Then, the total mass of compound powder was calculated to produce the mass of each material. Meanwhile, in the volume ratio method, the density of each material in the compound was used to calculate the required amount of each compound. Samples were then compressed under varied pressure, temperature and time to obtain optimization. Compositions of samples were confirmed using the Energy Dispersive Spectroscopy (EDS) while Seebeck and resistivity samples were measured using an in-house hot probe and 4-point probe. This study successfully fabricated Bi_2Te_3 and PbTe based bulk thermoelectric materials using the hot press method. Samples using atomic mass (AM) calculation show the closest composition ratio of n- $\text{Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$, p- $\text{Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$, n- $\text{Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$ and p- $\text{Pb}_{0.7}\text{Sn}_{0.2}\text{Te}_{1.1}$ which fabricated under pressure and holding time of 13 MPa and 17 minutes at a temperature of 423 K and 493 K respectively. Seebeck for n- $\text{Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$ at room temperature is $-53 \mu\text{V/K}$ which gives 65% lower compared to the literature composition of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ but n- $\text{Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$ samples give similar Seebeck of $-249 \mu\text{V/K}$. Similar results were obtained for both p- $\text{Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$ and p- $\text{Pb}_{0.5}\text{Sn}_{0.2}\text{Te}_{1.1}$ samples which shows a significant difference in ΔT as compared to $s\Delta T$ of literature. On the other hand, all samples showed slightly higher electrical resistivity than in the literature also has been discussed. It can be concluded that thermoelectric materials could be fabricated using the hot press method as an alternative method at a lower cost. Although its performance is lower than the SPS method, it could be improved by increasing the temperature, pressure and time. The implication of this study could encourage high-performance thermoelectric materials study in Malaysia and develop an interest in waste heat recovery.

الملخص

تعتبر المواد الكهروحرارية مفيدة في تحويل النفايات الحرارية إلى كهرباء طالما يوجد فرق في درجة الحرارة (ΔT). تعتبر المواد الكهروحرارية القائمة على البزموت تيلورايد (Bi_2Te_3) وتيلورايد الرصاص (PbTe) من أحدث المواد في نطاق درجات حرارة منخفضة ومتوسطة تتراوح بين 300-500 كلفن و 500-900 كلفن ، على التوالي. معامل سيبك هو أحد الخواص الكهروحرارية التي تحدد أدائه من خلال شخصية بلا أبعاد (ZT). طريقة التصنيع الشائعة لمواد TE هي تليد شرارة البلازما (SPS) تحت ضغط عالٍ (20 إلى 50 ميجا باسكال) ، ودرجة حرارة (773 إلى 1373 كلفن) وتحت تدفق التيار بسبب الأداء العالي الناتج ووقت قصير (من 5 إلى 30 دقيقة). ومع ذلك ، فإن المعدات غير متوفرة في ماليزيا. من ناحية أخرى ، يتم قياس قياس Seebeck الذي يتم إجراؤه تقليديًا باستخدام مسبار ساخن تحت اختلاف بسيط في درجة الحرارة ($s\Delta T$) والذي لا يمثل الحالة الحقيقية لتشغيل المادة. لذلك ، تهدف هذه الدراسة إلى التحقيق في طريقة تصنيع بديلة باستخدام آلة ضغط ساخن متاحة على نطاق واسع ودراسة سلوك سيبك تحت اختلافات كبيرة في درجات الحرارة (ΔT). تم عمل أربعة أنواع من العينات المستهدفة باستخدام هذه الطريقة ، وهي $\text{n-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ و $\text{n-PbTe}_{0.8}\text{Se}_{0.2}$ و $\text{p-Pb}_{0.4}\text{Sn}_{0.6}\text{Te}$ و $\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3$. تم دراسة طريقتين لتحضير العينة باستخدام طريقة نسبة الكتلة الذرية والحجم. في طريقة الكتلة الذرية ، تم حساب الوزن الجزيئي الكلي للمركب متبوعًا بنسبة الكتلة المثوية لكل مادة للحصول على الكثافة الإجمالية للمركب. ثم تم حساب الكتلة الكلية للمسحوق المركب لإنتاج كتلة كل مادة. وفي الوقت نفسه ، في طريقة نسبة الحجم ، تم استخدام كثافة كل مادة في المركب لحساب الكمية المطلوبة لكل مركب. تم بعد ذلك ضغط العينات تحت ضغط ودرجة حرارة ووقت متنوع للحصول على التحسين. تم تأكيد تكوين العينات باستخدام التحليل الطيفي للتشتت للطاقة (EDS) بينما تم قياس عينات سيبك وعينات المقاومة باستخدام مسبار ساخن داخلي ومسبار من 4 نقاط. نجحت هذه الدراسة في تصنيع المواد الكهروحرارية السائبة القائمة على PbTe و Bi_2Te_3 باستخدام طريقة الضغط الساخن. تُظهر العينات باستخدام حساب الكتلة الذرية (AM) أقرب نسبة تكوين لـ $\text{n-Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$ ، $\text{p-Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$ ، $\text{n-Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$ و $\text{p-Pb}_{0.7}\text{Sn}_{0.2}\text{Te}_{1.1}$ والتي تم تصنيعها تحت ضغط وقوة تحمل 13 ميجا باسكال و 17 دقيقة عند درجة حرارة 423 كلفن و 493 كلفن على التوالي. Seebeck لـ $\text{n-Bi}_{2.2}\text{Te}_{2.6}\text{Se}_{0.2}$ عند درجة حرارة الغرفة هي -53 V / K مما يعطي 65% أقل مقارنة بتركيبية الأدب لـ $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ لكن

عينات $n\text{-Pb}_{1.1}\text{Te}_{0.7}\text{Se}_{0.2}$ تعطي عينات مماثلة لـ Seebeck من $-249 \mu\text{V} / \text{K}$. تم الحصول على نتائج مماثلة لكل من عينات $p\text{-Bi}_{0.6}\text{Sb}_{1.6}\text{Te}_{2.8}$ و $p\text{-Pb}_{0.5}\text{Sn}_{0.2}\text{Te}_{1.1}$ والتي تظهر فرقاً كبيراً في ΔT مقارنةً بـ ΔT_s من الأدبيات. من ناحية أخرى ، أظهرت جميع العينات مقاومة كهربائية أعلى قليلاً مما كانت عليه في الأدبيات التي تمت مناقشتها أيضاً. يمكن استنتاج أن المواد الكهروحرارية يمكن تصنيعها باستخدام طريقة الضغط الساخن كطريقة بديلة وبتكلفة أقل. على الرغم من أن أدائها أقل من طريقة SPS ، إلا أنه يمكن تحسينها عن طريق زيادة درجة الحرارة والضغط والوقت. يمكن أن تؤدي الآثار المترتبة على هذه الدراسة إلى تشجيع دراسة المواد الكهروحرارية عالية الأداء في ماليزيا وتطوير الاهتمام باستعادة الحرارة المهدرة.

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LIST OF ABBREVIATIONS

ZT	Dimensionless Figure-of-Merit
ρ	Electrical resistivity
α	Seebeck coefficient
T	Absolute temperature
ρ	Electrical Resistivity
TEG	Thermoelectric Generator
Bi_2Te_3	Bismuth Telluride
PbTe	Lead Telluride
SPS	Spark Plasma Sintering
LAT	Large Temperature Difference
sAT	Small Temperature Difference
OTEC	Ocean Thermal Electric Conversion
h^+	Holes
e^-	Electron
ΔT	Temperature Difference
ΔV	Voltage Difference
Q	Amount of Heat
I	Electric Current
π_{ab}	Peltier Coefficient
Σ	Thomson Coefficient
Si	Silicon
Cu_2Se	Copper Selenide
SnSe	Tin Selenide
Ge	Germanium
PANI	Polyaniline
PEDOT	Poly (3,4-ethylene dioxythiophene)
PSS	Polystyrene sulfonate
CPs	Coordination Polymers
SiGe	Silicon-Germanium
STEG	Segmented Thermoelectric Generator
CTEG	Cascaded Thermoelectric Generator

TE	Thermoelectric
TECs	Thermoelectric Coolers
O ₂	Oxygen
PAS	Plasma-Activated Sintering
v	Volume
r	Radius
h	Height
ρ	Density
m	Mass
UKM	Universiti Kebangsaan Malaysia
USIM	Universiti Sains Islam Malaysia
EDS	Energy Dispersive Spectroscopy
SEM	Scanning Electron Microscope